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<b>14. ABSTRACT</b> This research project explored the utility of molecular precursor decomposition in superheated non-aqueous solvents directed towards semiconductor crystal growth. Reactions were run in toluene, THF, and under solvent free conditions. An <i>in situ</i> precursor synthesis and decomposition resulted in GaN nanoparticles from simple starting materials (GaCl <sub>3</sub> and NaN <sub>3</sub> ). Particle sizes range from about 10 to hundreds of nanometers. Upon annealing to 1000 °C, the poorly crystalline products ordered into crystalline hexagonal GaN and luminescence. The conversion of synthesized organometallic dimeric gallium amido precursors to GaN was less successful; however they showed some utility in vapor phase film growth. Silver and silver sulfide nanoparticles were also produced in a solvothermal system via silver azide decomposition producing particles in the 100 nm to micron size regime.							
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## **Final Performance and Technical Report**

**Contract Number:** N00014-99-1-0953

**Principal Investigator:** Edward G. Gillan

**Project Title:** Solvothermal Molecular Precursor Routes to Semiconductor Film and Crystal Growth

**Project Location:** University of Iowa, Iowa City, Iowa

**ONR Program Manager:** Stephen W. McElvany

### **Technical Objectives**

The objective of this project was to examine the utility of molecular single-source precursors and non-aqueous solvothermal media in the growth of crystalline compound semiconductor materials. Our near-term goal was to design and perfect synthetic methodologies that will allow us to grow crystals and nanocrystals of Group 13 nitride semiconductors with control over crystal morphology and size. We believe that molecular-based solution decomposition routes may be tailored through the use of catalysts and chemical additives to allow a degree of morphological control that is not easily attained by conventional synthetic routes. Solution decomposition methods are also amenable to nanocrystalline solid growth. A long-term goal is to design a non-aqueous route to crystalline compound semiconductors such as GaN for use as lattice-matched substrates in optoelectronic devices.

### **Technical Approach**

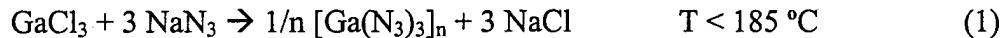
Molecular single-source precursors contain direct molecular bonds that mimic the bonding in the targeted solid-state material. In our studies, these precursors are synthesized by conventional bench top Schlenk chemistry or formed *in situ* in the solvothermal reactor. We examined both of these approaches at preforming bonds that will persist in the crystalline solid product. This approach is most often utilized in gas-phase reactions to form thin films, e.g. GaN from  $\text{Ga}(\text{N}(\text{CH}_3)_2)_3$  or gallium hydrazine derivatives. We also synthesized new molecular precursors that may help facilitate product formation at lower temperatures via decomposition in superheated non-aqueous (organic) solutions. These conversion reactions were performed in high-pressure steel reactors at temperatures up to 350 °C. Alkyl amines and ammonium salts were added to organic solutions (e.g., toluene, THF, pyridine) containing the precursors to determine their effects on decomposition and semiconductor crystallization.

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## Project Results

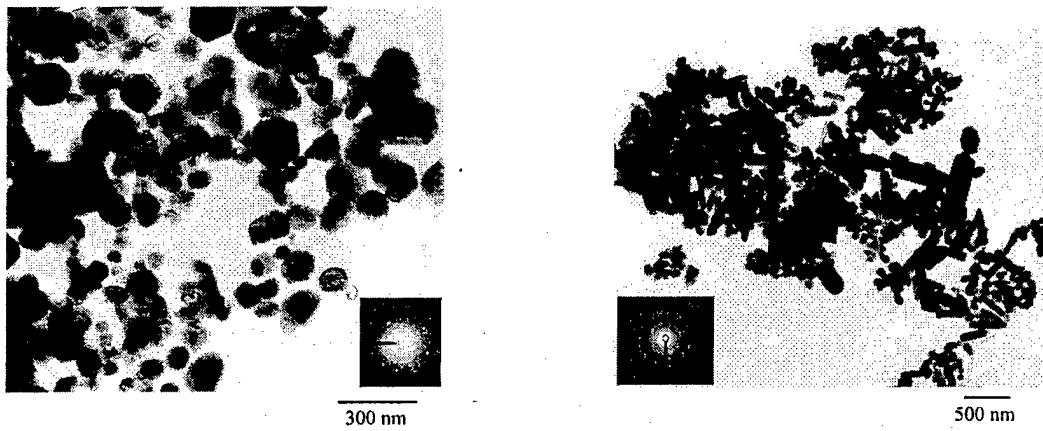
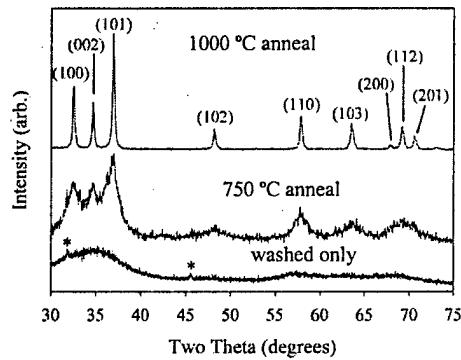
### A. Solvothermal GaN synthesis

We found distinct differences in the growth of GaN nanoparticles from the reaction of  $\text{GaCl}_3$  and  $\text{NaN}_3$  in aromatic non-coordinating (toluene) versus coordinating (THF) solvents. The overall proposed chemical reactions are noted below:



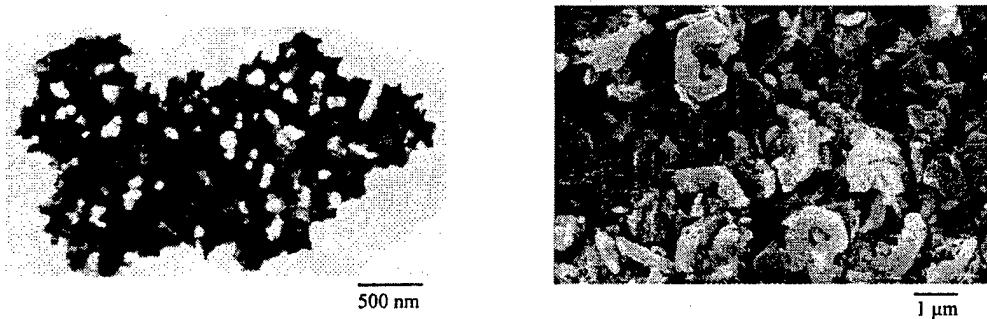
The THF solvent system facilitated azide decomposition, as evidenced by a significant increase in gas pressure, at temperatures lower than for toluene ( $220 \text{ }^\circ\text{C}$  versus  $260 \text{ }^\circ\text{C}$ , internal temperature). This may be due to an increase in soluble gallium azides generated in superheated THF, which are likely more susceptible to decomposition. In addition, THF will dissolve NaCl and increase contact with Ga-N components during the reaction.

The as-synthesized products and vacuum annealed systems show strong IR signatures for Ga-N bonding ( $570 \text{ cm}^{-1}$  absorbance) and no Ga-O features. There are also distinct C-C and C-H stretches in the as-synthesized and washed products, indicating that organic surface species and azide or  $\text{N}=\text{C}=\text{N}$  residues are present on the particle surfaces. While as-synthesized GaN is poorly crystalline, it anneals readily to the hexagonal phase by  $1000 \text{ }^\circ\text{C}$  and produces faceted crystallites (see figure at right and Figure 1). We observed long nanorod structures in toluene reaction products. After washing with water, these annealed nanorods become smaller and segmented and are readily observed as crystalline GaN by TEM (see Figure 1 right). Nanoparticles are also observed in these systems.



**Figure 1.** TEM results for crystalline hexagonal GaN nanoparticles produced upon annealing solvothermal reaction products to  $1000 \text{ }^\circ\text{C}$  under vacuum.

Scanning electron microscopy (SEM) of THF products shows distinct micron sized blocks of NaCl indicating that this coordinating solvent dissolves the salt during the reaction. Washed GaN THF products also have an agglomerated/fused architecture, suggesting that the GaN nanoparticles grow together because the byproduct salt is removed by the solvent (Figure 2 left). The THF materials exhibit similar crystallization properties, however larger coherent hexagonally faceted crystals are observed by microscopy after annealing (Figure 2 right). This enhanced cohesion may be due to the initially agglomerated nature of the as-synthesized product as noted above. The line broadening of GaN X-ray diffraction peaks indicates that the crystallites are less than 100 nm for annealed samples from toluene and THF, however THF produces larger crystalline domains.



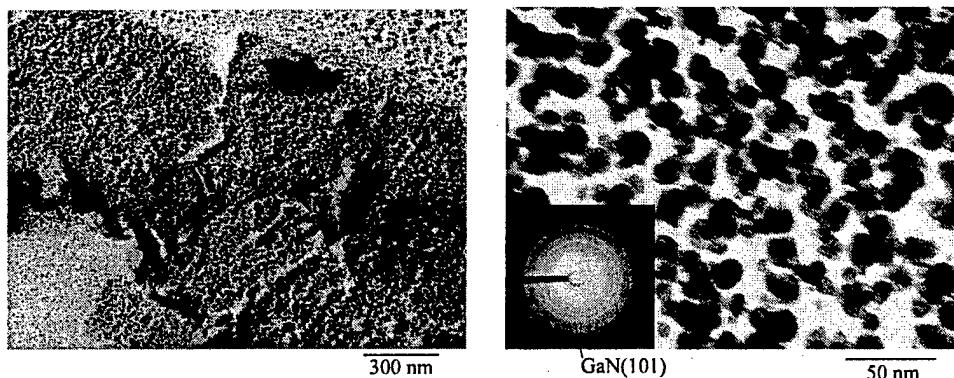
**Figure 2.** Electron microscopy of GaN materials from solvothermal THF reactions before annealing (left, TEM) and after annealing (right, SEM).

Our initial studies on solvothermal reactions between  $\text{GaCl}_3$  and  $\text{NaN}_3$  were published in 2001 (*Chem. Mater.* 2001, 13, 4290-4296). We have recently begun to modify this synthetic strategy using other nitrogen sources, e.g.  $\text{LiNH}_2$  and  $\text{NaNH}_2$ , in place of  $\text{NaN}_3$ . The toluene solvothermal reactions appear most successful in this regard, producing amorphous GaN materials that crystallize upon annealing. In the case of strongly coordinating solvents such as THF and  $\text{Et}_2\text{NH}$ , the products appear to somewhat oligomeric and have a stronger tendency to sublime during annealing. We examined whether a mixed toluene/ $\text{Et}_2\text{NH}$  system will facilitate product recrystallization and crystal growth in the solvothermal environment. We have also begun studies on the addition of external seed crystals (e.g.,  $\text{Al}_2\text{O}_3$  powder and Si wafers) to the  $\text{GaCl}_3/\text{NaN}_3$  reaction, in order to examine templated growth effects.

We performed preliminary examinations on the *in situ* formation of solid solution nitrides by adding 25-50 at% aluminum and indium halides ( $\text{AlCl}_3$ ,  $\text{InCl}_3$ , and  $\text{InBr}_3$ ) to our GaN solvothermal reaction. In the case of  $\text{InBr}_3$  additions in THF reactions with  $\text{GaCl}_3/\text{NaN}_3$ , solid-solution salt byproducts,  $\text{NaCl}_x\text{Br}_{1-x}$ , were observed along with indium metal. While we have indirect indications that some indium is incorporated in the GaN structure, the product is unstable to annealing, so we have not been able to verify this by diffraction methods. In some of these solid solution reactions, unusual long rod-like morphologies are observed along with indium spheres. The aluminum addition reactions show clearer indications of some solid-solution formation, as evidenced by asymmetric GaN peak broadening and shifts in d spacings.

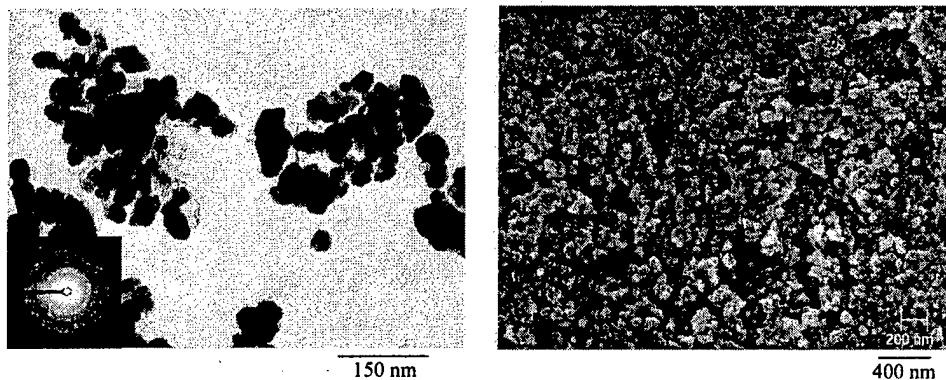
*B. Solvent-free (azidothermal) GaN synthesis*

Since the azide ligand proved to be successful in generating nitrogen-containing materials, we examined whether a solvent free reaction between molten  $\text{GaCl}_3$  and  $\text{NaN}_3$  was feasible. With a careful control of temperature, this reaction works very well and produced bright orange air-stable products. The byproduct salt is easily removed with glycerol/ethanol, leaving small GaN nanoparticles (Figure 3).



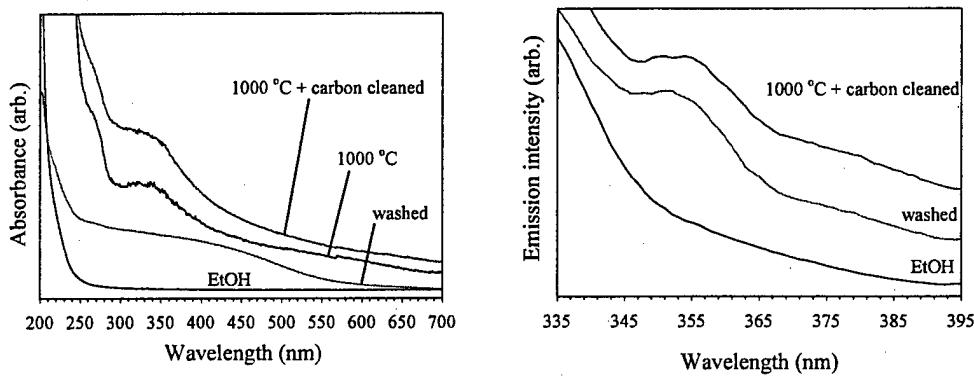
**Figure 3.** Transmission electron microscopy images of washed products from the solvent-free reaction of  $\text{GaCl}_3$  and  $\text{NaN}_3$  at 210 °C. All unindexed diffraction rings correspond to residual NaCl.

When this material is annealed the surface glycerol turns to carbon and prevents grain/particle growth, leading to carbon-coated 50 nm crystalline GaN (Figure 4). The carbon coating can be carefully removed at 500 °C in air, leaving yellow GaN powder. A account of this work was published in in 2002 (*Nano Lett.* 2002, 2, 899-902).



**Figure 4.** Electron microscopy images of solvent-free GaN annealed at 1000 °C.

As shown in Figure 5, the as-synthesized and washed GaN particles from solvent-free synthesis have optical absorption and emission characteristics consistent with GaN properties ( $E_g = 3.4$  eV, 365 nm).

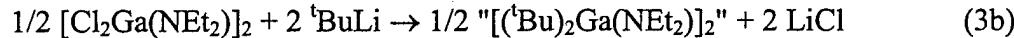
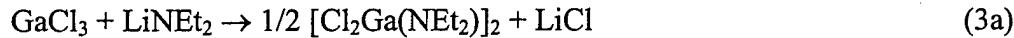


**Figure 5.** Optical absorption and emission properties ( $E_{\text{ex}} = 300 \text{ nm}$ ) of solvent-free GaN.

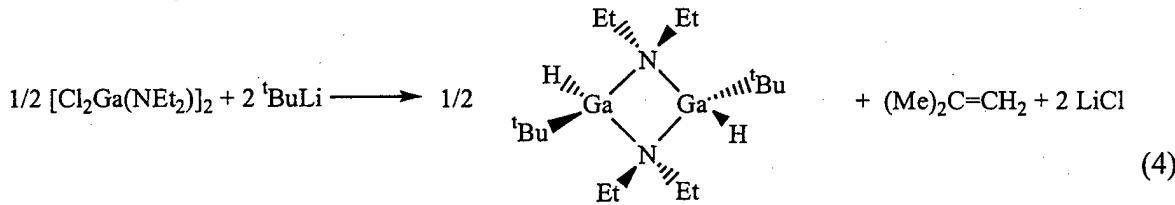
We are currently exploring the surface derivatization of GaN nanoparticles for the purpose of patterning them on surfaces or for use as luminescent probes. Since GaN is oxidatively sensitive, these organic surface coatings may also improve long-term air storage capabilities.

### C. Organometallic gallium dimeric amino precursors

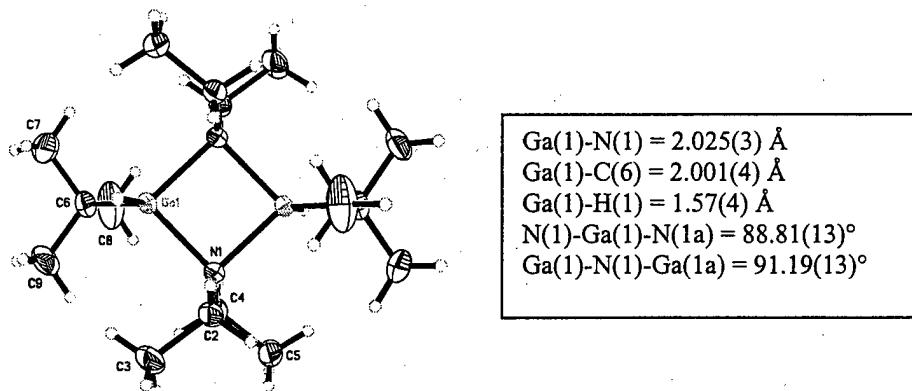
We have synthesized a variety of dimeric compounds containing  $\text{Ga}_2\text{N}_2$  core ring structures including  $[{}^t\text{Bu}(\text{H})\text{Ga}(\mu\text{-NEt}_2)]_2$ ,  $[{}^t\text{Bu}(\text{Cl})\text{Ga}(\mu\text{-NEt}_2)]_2$ ,  $[{}^t\text{Bu}(\text{Cl})\text{Ga}(\mu\text{-NEt}_2)_2\text{GaCl}_2]$ , and  $\text{GaCl}_{3-x}(\text{NH}{}^t\text{Bu})_x$  compounds. The synthesis of the final product,  $[{}^t\text{Bu}(\text{H})\text{Ga}(\mu\text{-NEt}_2)]_2$ , was achieved in a one-pot reaction where  $\text{GaCl}_3$  was reacted with  $\text{LiNEt}_2$  (Eqn. 3a) and then reacted with 2 equivalents of  ${}^t\text{BuLi}$  (Eqn. 3b).



The  $^1\text{H}$  NMR and MS data on the isolated product from (3b) strongly indicated that this dimeric molecular solid contained one  $\text{Ga-}{}^t\text{Bu}$  and one  $\text{Ga-H}$  bond per gallium center. A room temperature reaction in an NMR tube demonstrated that isobutylene,  $(\text{Me})_2\text{C=CH}_2$ , was formed as a byproduct of (3b). This suggests that  $\beta$ -hydride elimination occurred during synthesis. The above evidence coupled with elemental analysis yields a formulation of  $[({}^t\text{Bu})\text{HGa}(\text{NEt}_2)]_2$  for the isolated crystalline solid (Eqn. 4).

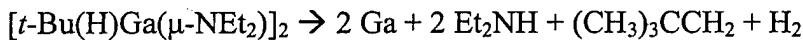


X-ray diffraction studies on single crystals of  $[({}^t\text{Bu})\text{HGa}(\text{NEt}_2)]_2$  showed that the molecular geometry was close to that shown in (4) with an inversion center and a  $\text{Ga}_2\text{N}_2$  core that deviates only a few degrees from a  $90^\circ$  square. The data set was of reasonable quality to refine the hydride position and determine that the  $\text{Ga-H}$  bond is approximately  $1.57 \text{\AA}$  (Figure 6).



**Figure 6.** Structural drawing of  $[t\text{-Bu}(\text{H})\text{Ga}(\mu\text{-NEt}_2)]_2$  based on single-crystal X-ray analysis.

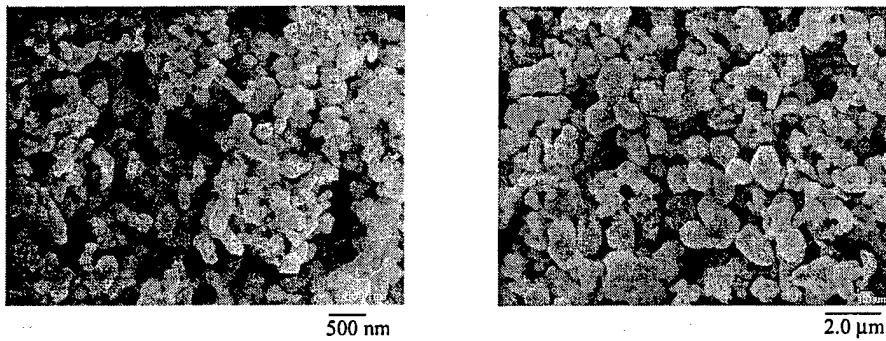
We examined this molecular precursor for the low-temperature growth of GaN films by chemical vapor deposition (CVD). The precursor deposited films by 250 °C; however our analysis indicates that the amorphous films are very gallium-rich and most of the nitrogen was lost as volatile diethylamine:



The physical and chemical properties of this new gallium hydride and those of related derivatives were recently published in 2002 (*Inorg. Chem.* 2002, 41, 2920-2926). We are examining whether hydrazine derivatives may prove more useful as CVD and solvothermal precursors.

#### D. Silver and $\text{Ag}_2\text{S}$ solvothermal synthesis

We have recently extended the solvothermal azide decomposition method to transition metal and metal sulfide growth. Specifically the decomposition of  $\text{AgN}_3$  in toluene, THF, and trioctylamine was investigated. It was observed that nitrogen gas evolution occurs near 200 °C and produces silver particles from 200 nm - 1 μm in size. The smaller crystalline Ag particles are produced from the coordinating solvents (Figure 7 left). When sulfur was dissolved in THF, the  $\text{AgN}_3$  decomposition temperature was lowered below 100 °C and resulting in crystalline sub-micron  $\text{Ag}_2\text{S}$  particles (Figure 7 right). An article detailing this work is in press in *Materials Research Bulletin*.



**Figure 7.** Products from  $\text{AgN}_3/\text{THF}$  reactions forming Ag particles (left) and with S to form  $\text{Ag}_2\text{S}$  particles (right).